

# -sizing composition for an insulation product based on mineral wool, and resulting products

The present invention relates to the manufacture of  
 5 insulation products, especially thermal and/or acoustic  
 insulation products, based on mineral wool. More  
 precisely, it relates to an improved sizing composition  
 based on an epoxy resin allowing the mechanical  
 strength of such products after ageing, especially in a  
 10 wet environment, to be increased.

Insulation products based on mineral wool, especially  
 glass or rock wool, generally take the form of  
 relatively rigid panels, shelves, wound felts or even  
 15 veils. They are intended in particular for the thermal  
 and/or acoustic insulation of buildings.

The manufacture of such products comprises a first step  
 of manufacturing the wool itself, especially using the  
 20 technique known as centrifugal attenuation, in which  
 the molten mineral material is converted into  
 filaments, and a forming step in which the filaments  
 are attenuated and entrained towards a receiving member  
 by a high-temperature high-speed gas stream in order to  
 25 form a sheet thereon. In order to ensure cohesion of  
 the sheet, a sizing composition, which contains a  
 thermosetting resin, is sprayed onto the wool as it  
 travels towards the receiving member. The sheet thus  
 treated is then subjected to a heat treatment in an  
 30 oven in order to cure the resin and obtain a product  
 having the desired properties, such as dimensional  
 stability, tensile strength, tear resistance, puncture  
 resistance, thickness recovery after compression, and  
 homogeneous colour.

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In the insulation product, the binder has the function  
 of binding the fibres together - it must adhere  
 correctly to the glass and spread uniformly over the  
 fibres so as thereafter to be preferably at the

junction points between the fibres and thus allow a resilient fibrous sheet to be obtained.

The sizing composition is therefore preferably sprayed  
5 when the fibres are still separate fibres, that is to say before formation of the sheet. Consequently, the size is sprayed in the fibre-receiving hopper, beneath the burners that generate the attenuating gas stream. This therefore precludes the use of inflammable organic  
10 solvents and/or contaminants for formulating the size, the risk of a fire and/or of contamination in the receiving hopper being too high.

In addition, the resin serving as binder, although it  
15 must not cure too rapidly before sheet formation, it must also not have too long a cure time. By controlling this time, the risks of pregelling are thus avoided and the cure time remains compatible with high production rates, especially by taking measures to ensure that the  
20 binder has completely cured after the high-temperature oven treatment (around 260°C).

The most commonly used sizes contain a thermosetting resin of the resol type, obtained by condensation of a  
25 phenol with a formaldehyde, or equivalents, in the presence of a basic accelerator, water as dilution agent, urea, serving to reduce the amount of free formaldehyde and also acting as binder, and various additives, such as aqueous ammonia, oil, coupling  
30 agents, for coupling to the glass, colorants and, optionally, fillers.

Although this type of size does allow a high level of mechanical performance to be achieved, its use,  
35 especially during the oven treatment, generates undesirable gaseous emissions, for example of formaldehyde, ammonia and other volatile organic compounds.

To alleviate this drawback, sizing compositions have been proposed that are based on an epoxy resin of the glycidyl ether type and a non-volatile amine hardener (see EP-A-0 369 848 and FR 02/08873). This solution  
5 makes it possible for the emissions to be very substantially reduced, both during manufacture of the insulation product, since complete cure can be achieved at a lower temperature (around 220°C), and during its use at high temperatures, above 150°C and up to 700°C.

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Although it is important for the mechanical properties of the insulation product to be satisfactory after manufacture and up till its use, in order to ensure that it is properly installed on the site, it is also  
15 desirable for them to be maintained for a certain time once the product is in place, in order to guarantee that it has a sufficient lifetime.

For the most part, insulation products have to be  
20 subjected, as they age, to thermal cycles of relatively large amplitude and variable condensation conditions that result in them being exposed to moisture, which entails a loss of their mechanical properties. Such losses may be large when the mineral wool is  
25 particularly water-sensitive, for example when it is a wool that can dissolve in a physiological medium.

The object of the invention is to remedy these drawbacks and to improve the mechanical strength after  
30 ageing, especially in a wet environment, of insulation products based on mineral wool provided with an epoxy binder, that is to say to reduce the losses in mechanical properties of these products after ageing, especially in a wet environment.

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This object is achieved according to the invention by means of a sizing composition based on an epoxy resin of the glycidyl ether type and an amine hardener, this composition being characterized in that it furthermore

includes an accelerator chosen from imidazoles, imidazolines and mixtures thereof.

5 The term "accelerator" here has the usual meaning in the field of chemistry and denotes a compound that increases the rate of reaction between the epoxy resin and the amine hardener.

10 The size makes it possible for the losses in properties after ageing, particularly wet ageing, to be markedly reduced compared with a similar product not containing the accelerator, without significantly modifying these properties just after manufacture.

15 Another subject of the invention is a process for manufacturing an insulation product employing the aforementioned sizing composition.

20 A further subject of the invention is the insulation products coated with the said sizing composition.

25 The epoxy resin according to the invention is obtained by the reaction of epichlorohydrin with an alcohol. Preferably, the alcohol is a polyol comprising at least two hydroxyl functional groups per molecule and at most 100, preferably at most 50 and better still at most 10 hydroxyl functional groups per molecule. Particularly preferably, the alcohol is a diol.

30 Advantageously, the resin has an EEW (Epoxy Equivalent Weight) corresponding to the mass of resin, in grams, containing one gram-equivalent of epoxide functional groups, which is between 150 and 2000, preferably between 160 and 700 and better still at most equal to 35 300. Such a resin has the advantage of generating a small amount of undesirable emissions during the fibrizing operation and the subsequent oven treatment, and it also remains compatible with the known processes for spraying the size onto the fibres for the purpose

of forming insulation products.

Also advantageously, the resin has a functionality (number of epoxide groups per molecule) of at least 2  
5 and preferably less than 10.

The epoxy resin according to the invention is water-dispersible or capable of being emulsified in the presence of an emulsifying agent or a dispersing agent.  
10 This is because it is essential for the resin to have at least one of these properties so that the sizing composition can be sprayed properly. In this regard, sprayability is dependent on the water dilutability of the resin, defined as follows: the water dilutability  
15 of an epoxy resin emulsion or dispersion is the volume of deionized water that can be added, at a given temperature, to unit volume of this composition before the emulsion or dispersion "breaks", that is to say before the said emulsion or dispersion becomes  
20 destabilized or has undergone phase separation. The water dilutability of a resin that can be used in a sprayable sizing composition is advantageously at least 500%, preferably 1000%, at 20°C.

25 Preferably, the epoxy resin is chosen from resins resulting from the reaction between epichlorohydrin and bisphenol A, bisphenol F, polyethylene glycols, glycerol, pentaerythritol and novolac resins, and mixtures of these resins. The resins formed by a  
30 reaction between epichlorohydrin and bisphenol A are particularly preferred.

As examples of such resins, mention may be made of:

- 35 - resins in aqueous emulsion, sold by Resolution under the names Epi-Rez® 5003-w-55 (EEW = 195-215), Epi-Rez® 3510-w-60 (EEW = 185-215), Epi-Rez® 3515-w-60 (EEW = 225-275), and Epi-Rez® 3522-w-60 (EEW = 615-715;
- resins that can be emulsified in water, sold by Resolution under the names Epikote® 828 (EEW = 184-

190), and Epikote® 255 (EEW = 193-205) or by Dow Chemical under the names DER 330 (EEW = 176-185) and DER 331 (EEW = 182-192).

5 Other epoxy compounds of the glycidyl ether type may be added to the sizing composition. As examples, mention may be made of epoxidized aliphatic compounds and epoxidized fatty alcohols, useful especially for modifying the viscosity of the size, and epoxy resins  
10 of the halogenated glycidyl ether type, especially derivatives of dibromophenyl glycidyl ethers, such as dibromophenyl glycidyl ether, 2-methyl-4,6-dibromophenyl glycidyl ether, 4-methyl-2,6-dibromophenyl glycidyl ether and 4-cumyl-2,6-dibromophenyl glycidyl  
15 ether, which make it possible in particular to give the product better high-temperature resistance. The content of these compounds generally represents less than 30%, preferably less than 10%, by weight of the epoxy resin.

20 The amine hardener according to the invention is generally chosen from aliphatic polyamines, such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and polyglycoldiamines, cycloaliphatic polyamines, such as  
25 1,3-bis(aminomethyl)cyclohexane, 4,4-diaminocyclohexylmethane, methylenediamine and 2,4-diaminocyclohexanol, and aromatic polyamines, such as m-phenylenediamine, m-xylylenediamine, diethyltoluenediamine, diamino-diphenylsulphone and dicyandiamine.

30 The amount of amine hardener to be introduced into the sizing composition depends on the number of amine reactive sites carried by the molecule. Preferably, the hardener has an amine equivalent weight/H ratio defined  
35 as the ratio of the amine molecular weight to the number of active hydrogen atoms, which is between 20 and 300. Preferably, the amount of hardener is introduced in stoichiometric amount relative to the resin so as to avoid an excess of hardener which may

lead to the emission of volatile products on the fibre-receiving belt and/or in the oven.

Also preferably, the hardener is non-volatile, that is  
5 to say that, under the spraying conditions, it cannot undergo spontaneous ignition. The flashpoint of the hardener is advantageously above 150°C and better still above 180°C.

10 The sizing composition furthermore includes an accelerator chosen from imidazoles, imidazolines and mixtures thereof. Choosing the accelerator from within a limited family of compounds makes it possible to achieve the desired performance in terms of ageing  
15 resistance, especially in a wet environment.

As examples of imidazoles, mention may be made of imidazole, 1-methylimidazole, 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole and  
20 4,4'-methylenebis(2-ethyl-5-methylimidazole).

As an example of an imidazoline, mention may be made of 2-ethyl-N-phenylimidazoline.

25 Preferably, 2-methylimidazole is used.

Generally, the accelerator is introduced into the sizing composition in an amount of 0.1 to 5 parts, preferably 0.5 to 3 parts and better still 0.5 to 2  
30 parts, by weight of dry matter per 100 parts by weight of dry matter of epoxy resin/hardener.

The sizing composition may furthermore include the following additives, per 100 parts by weight of dry  
35 matter of resin/hardener:

- 0 to 2 parts, preferably around 0.5 parts, of a coupling agent such as a silane;
- 0 to 20 parts, preferably 6 to 15 parts, of an oil.

The well-known role of the aforementioned additives will be briefly recalled here:

- 5       - the water has a lubricating role and makes it possible to adjust the viscosity to the spraying conditions, to cool the fibres and limit pregelling effects;
- 10       - the coupling agent ensures bonding between the mineral fibre and the cured binder. It helps to increase the mechanical properties and contributes to improving the ageing resistance. The silane is generally an amino silane, preferably  $\gamma$ -aminopropyltriethoxysilane; and
- 15       - the oil lubricates the fibres, helps to reduce dust liable to be generated when handling the finished products (for example insulating sheets) and improves the feel. It is generally inert with respect to the other constituents and can be emulsified in water. Usually, it is an oil consisting of hydrocarbons
- 20       extracted from petroleum.

The subject of the invention is also a process for manufacturing a thermal and/or acoustic insulation product, based on mineral wool provided with an epoxy binder, exhibiting better mechanical resistance after

25       ageing, especially in a wet environment, in which process:

- a) mineral fibres are formed from a molten mineral composition;
- 30       b) a sizing composition, comprising an epoxy resin of the glycidyl ether type, an amine hardener and an accelerator chosen from imidazoles, imidazolines and mixtures thereof, is sprayed onto the fibres obtained at a);
- 35       c) the fibres are collected in the form of a sheet; and
- d) the sheet is subjected to a heat treatment at a temperature below about 260°C, preferably around 220 to 240°C.

In general, it is necessary for the sizing composition to have a pot life compatible with the spraying conditions and for it not to cure before sheet  
5 formation. This means, in other words, that there must be as little pregelling of the size as possible.

Given that the rate of reaction between the amine functional groups of the hardener and the epoxide  
10 functional groups increases very rapidly in the presence of the accelerator, preparation of the size by mixing, even extemporaneously, the epoxy resin, the amine hardener, the accelerator and optionally, the additives prior to spraying is to be avoided in order  
15 to prevent any risk of the spray ring becoming blocked.

It is preferred to spray the size onto the fibres according to the following two methods of  
20 implementation.

In a first method of implementation, the accelerator is mixed with the other constituents of the size, preferably upstream of the spray ring and as late as possible, and then the size is applied in the usual  
25 manner to the mineral wool. This method of implementation is advantageous when the rate of reaction between the epoxy resin and the amine hardener is low enough and does not cause premature gelling that may lead to total or partial blockage of the spray  
30 means.

According to a first variant, the accelerator is introduced into the mixture of the other constituents of the size, which constituents may be introduced  
35 separately or may have been mixed beforehand (forming a premix). It is preferred to introduce the accelerator into a premix containing all of the other constituents of the size.

According to a second variant, a first mixture, consisting of the accelerator and the amine hardener, is produced and a second mixture, consisting of the epoxy resin and the other constituents of the size, is produced, and then the said first and second mixtures are introduced before the spray ring.

In a second preferred method of implementation, valid even when the reactivity of the size is low, the accelerator is applied separately from the spraying of the other constituents of the size onto the fibres. For example, the accelerator in aqueous phase can be sprayed near the ring for spraying the other constituents of the size, especially by superposing two spray rings in the path of the mineral wool in the direction of the receiving member, one ring (preferably the first in the direction of advance of the wool) spraying the accelerator and the second one spraying the other constituents of the size.

The insulation products obtained according to one or other of the methods of implementation, which also constitute a subject of the invention, contain 0.5 to 15%, preferably 1 to 12%, by weight of cured binder relative to the total weight of mineral fibres. In its crosslinked form, the binder is solid, infusible and insoluble in water.

The products obtained are white in colour, if no colorant has been added.

The insulation products obtained may have the appearance of a sheet or a veil. They may be in the form of a panel of variable stiffness, a shell, or a roll (of felt or veil). Where appropriate, at least one of their faces is coated with a layer or film for protecting the mineral wool, for example a veil of mineral fibres, preferably glass fibres, or a sheet of kraft paper. Particularly preferably, the veil of

fibres has a weight of between 10 and 300 g/m<sup>2</sup> and contains at least 1%, preferably at least 2% and advantageously at least 4%, by weight of cured binder obtained from the size according to the invention.

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The products obtained within the context of the present invention are especially intended to form thermal and/or acoustic insulation products, in particular for buildings and for applications requiring high resistance to high temperatures (industrial shells and domestic ovens. They may also serve as substrates for soilless cultivation.

The following non-limiting examples illustrate the invention.

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#### EXAMPLE

Glass wool was manufactured using the internal centrifugal technique in which the molten glass composition was converted into fibres by means of a tool called a spinner, comprising a basket forming a chamber for receiving the molten composition and a peripheral band pierced by a multitude of holes. The spinner was rotated about its axis of symmetry, placed vertically, the composition was ejected through the holes under the effect of the centrifugal force, and the material escaping from the holes was attenuated into fibres with the assistance of an attenuation gas stream.

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In the conventional manner, a size spray ring was placed beneath the fibrizing spinner so as to spread the sizing composition uniformly over the glass wool as it was being formed.

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The mineral wool thus sized was collected on a belt conveyor equipped with internal suction boxes that held the mineral wool, in the form of a felt or sheet, on

the surface of the conveyor. The conveyor then ran through an oven maintained at 220°C in which the resin of the size was cured to form a binder.

5 The composition of the size was the following (in parts by weight of dry matter):

- epoxy resin of the glycidyl ether type:  
Epi-Rez® 3510-w-60 (from Resolution): 85 parts
- hardener: tetraethylenepentamine (TEPA) 15 parts
- 10 - accelerator: 2-methylimidazole 1 part
- coupling agent: Silquest® A1100  
(from Crompton) 0.5 parts
- oil: Mulrex® 88 (from Mobil) 9.5 parts

15 The size composition was sprayed under the following conditions: a first mixture, comprising the resin, the coupling agent and the oil, and a second mixture, comprising the hardener and the accelerator, were produced. These two mixtures were fed separately into  
20 the spray ring and combined just before their introduction into the said ring. The spray rate was set so as to deposit around 5% by weight of dry matter relative to the weight of glass wool.

25 Two control tests were carried out with a size not containing the accelerator, the first being treated in an oven at 220°C (Control 1) and the second at a temperature of 260°C (Control 2).

30 Another control test was also carried out with a size containing 2,4,6-tri(dimethylaminomethyl)phenol as accelerator (Control 3).

The tensile strength after manufacture ( $TS_{\text{man}}$ ) and the  
35 tensile strength after accelerated ageing in an autoclave at a temperature of 105°C and 100% relative humidity for 15 minutes ( $TS_{15}$ ) or 45 minutes ( $TS_{45}$ ) were measured on the product obtained.

The tensile strength TS was measured according to the ASTM C 686-71T standard on a specimen cut from the insulation product by stamping. The specimen had the shape of a torus 122 mm in length, 46 mm in width, a  
5 radius of curvature of the cut at the outer edge equal to 38 mm and a radius of curvature of the cut at the inner edge equal to 12.5 mm.

The specimen was placed between two cylindrical  
10 mandrels of a test machine, one of which was fixed and the other moved at a constant speed. The breaking force F (in grams force) of the specimen was measured and the tensile strength TS defined by the ratio of the breaking force F to the mass of the specimen was  
15 calculated.

The results are given in Table 1, which indicates, for each test, the percentage loss of tensile strength relative to the initial state after manufacture and the  
20 percentage improvement over the control containing no accelerator (the value in brackets).

The thickness recovery was measured on the product obtained, allowing the dimensional behaviour to be  
25 assessed. The procedure was as follows: the product was compressed with a degree of compression (defined as the ratio of the nominal thickness to the thickness under compression) of 6/1 for 1, 12 and 30 days. The thickness recovery corresponds to the ratio of the  
30 thickness after compression to the nominal thickness (expressed in per cent). The results are given in Table 1.

Table 1

	TS <sub>man</sub>	TS <sub>15</sub> (gForce/g)	Loss (%)	TS <sub>45</sub> (gForce/g)	Loss (%)	Thickness recovery (%)		
						1 d	12 d	30 d
<b>Example</b>	302 (-4.4%)	204 (+25.9%)	32.5	167 (+51.8%)	44.7	140	138	137
<b>Control 1</b>	316	162	48.7	110	65.2	137	136	136
<b>Control 2</b>	300	159	47.0	120	60.0	140	137	136
<b>Control 3</b>	301]	147	51.1	110]	63.5	141	139	138
<b>Control 4</b>	327	253	22.2	208	36.0	143	137	137

The results in Table 1 show that the product according to the invention (Example) has a better tensile strength than the equivalent product containing no accelerator (Control 1) and the percentage loss after ageing is less, whether after 15 minutes or 45 minutes of autoclave treatment.

Compared with the product containing no accelerator, the improvement in tensile strength of the highly aged products is equal to 51.8%, which represents a very substantial improvement.

It should be noted that the presence of the catalyst does not degrade the properties of the products according to the invention, whether as regards tensile strength after manufacture (TS<sub>man</sub>) or thickness recovery.

An improvement in tensile strength is not obtained with the conventional accelerator of Control 3. Nor does the higher curing temperature (of Control 2) make it possible to achieve a better tensile strength after ageing. For comparison, Table 1 indicates the tensile strength and thickness recovery values of a standard

product (Control 4) treated with a size incorporating a conventional phenol-formaldehyde resin in an oven at 260°C.

5 The size had the following composition (in parts by weight):

	- phenol-formaldehyde resin	55 parts
	- urea	45 parts
	- coupling agent (Silquest® A 1100)	0.5 parts
10	- oil (Mulrex® 88)	9 parts
	- ammonium sulphate	3 parts
	- aqueous ammonia (20% solution)	6 parts

The phenolic resin was of the type described in  
15 EP-A-0 148 050.

The product according to the invention does not have the level of performance of that containing a phenolic resin; nevertheless, it does constitute a good  
20 compromise as it reconciles good ageing resistance, especially in a wet environment, with a very low level of emissions of undesirable gases (which is not the case with phenolic resins, which release formaldehyde) and a lower energy cost, thanks to the use of ovens  
25 operating at lower temperature.